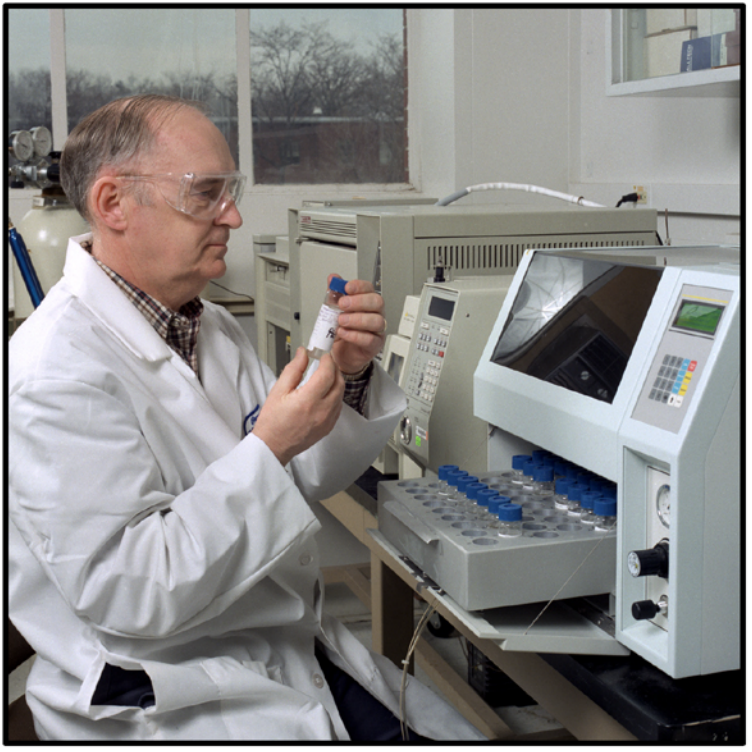
7. QUALITY ASSURANCE



7. QUALITY ASSURANCE

QA plans exist for both radiological and nonradiological analyses; these QA documents were prepared in accordance with DOE Order 5700.6C[29] and discuss who is responsible for QA and for auditing analyses. Both documents are supplemented by operating manuals.

7.1. Sample Collection

Many factors enter into an overall QA program other than the analytical quality control. Representative sampling is of prime importance. Appropriate sampling protocols are followed for each type of sampling being conducted. Water samples are pretreated in a manner designed to maintain the integrity of the analytical constituent. For example, samples for trace radionuclide analyses are acidified immediately after collection to prevent hydrolytic loss of metal ions and are filtered to reduce leaching from suspended solids.

The monitoring wells are sampled using the protocols listed in the *RCRA Ground-Water Monitoring Technical Enforcement Guidance Document*.[28] The volume of water in the casing is determined by measuring the water depth from the surface and the depth to the bottom of the well. This latter measurement also determines whether siltation has occurred that might restrict water movement in the screened area. For those wells in the glacial till that do not recharge rapidly, the well is emptied, and the volume removed is compared with the calculated volume. In most cases, these volumes are nearly identical. The well is then sampled by bailing with a Teflon bailer. If samples for parameters such as priority pollutants are collected, field parameters for these samples (pH, specific conductance, redox potential, and temperature) are measured per well volume while purging. For samples in the porous, saturated zone, which recharges rapidly, three well volumes are purged by using submersible pumps. If field parameters are measured, samples are collected as soon as these readings stabilize. All samples are placed in precleaned bottles, labeled, and preserved. All field measurement and sampling equipment is cleaned by field rinsing with Type II deionized water. The samples are transferred to the analytical laboratory via a computer floppy disk that generates a one-page list of all samples. This list acts as the chain of custody transfer document.

7.2. Radiochemical Analysis and Radioactivity Measurements

All nuclear instrumentation is calibrated with standard sources obtained from or traceable to the National Institute of Standards and Technology (NIST). The equipment is usually checked daily with secondary counting standards to ensure proper operation. Samples are periodically analyzed in duplicate or with the addition of known amounts of a radionuclide to check precision and accuracy. When a nuclide is not detected, the result is given as “less than” (<) the detection limit by the analytical method used. The detection limits are chosen so that the measurement uncertainty at the 95% confidence level is equal to the measured value. The air and water detection limits for all radionuclides for which measurements were made in 1999 are given in Table 7.1. The relative error

in a result decreases with increasing concentration. At a concentration equal to twice the detection limit, the error is approximately 50% of the measured value; at 10 times the detection limit, the error is approximately 10%.

Average values are usually accompanied by a plus-or-minus (±) limit value. Unless otherwise stated, this value is the standard error at the 95% confidence level calculated from the standard deviation of the average. The ± limit value is a measure of the range in the concentrations encountered at that location; it does not represent the conventional uncertainty in the average of repeated measurements on the same or identical samples. Because many of the variations observed in environmental radioactivity are not random but occur for specific reasons (e.g., seasonal variations), samples collected from the same location at different times are not replicates. The more random the variation in activity at a particular location, the closer the confidence limits will represent the actual distribution of values at that location. The averages and confidence limits should be interpreted with this in mind. When a ± value accompanies an individual result in this report, it represents the statistical counting error at the 95% confidence level.

TABLE 7.1

Air and Water Detection Limits

Nuclide or Activity	Air (fCi/m^3)	Water (pCi/L)
Americium-241	-[a]	0.001
Beryllium-7	5	-
Californium-249	-	0.001
Californium-252	-	0.001
Cesium-137	0.1	1
Curium-242	-	0.001
Curium-244	-	0.001
Hydrogen-3	-	100
Lead-210	1	-
Neptunium-237	-	0.001
Plutonium-238	0.0001	0.001
Plutonium-239	0.0001	0.001
Radium-226	-	0.1
Radium-228	-	0.1
Strontium-89	0.1	2
Strontium-90	0.01	0.25
Thorium-228	0.001	-
Thorium-230	0.001	-
Thorium-232	0.001	-
Uranium-234	0.001	0.01
Uranium-235	0.001	0.01
Uranium-238	0.001	0.01
Uranium - natural	0.02	0.2
Alpha	0.2	0.2
Beta	0.5	1

[a] A hyphen indicates that a value is not required.

ANL-E continues to participate in the DOE Environmental Measurements Laboratory Quality Assurance Program (DOE-EML-QAP), which consists of semiannual distribution of three different sample matrices containing various combinations of radionuclides that are analyzed. Table 7.2 summarizes the results for 1999. In the table, the EML value, which is the result of duplicate determinations by that laboratory, is compared with the average value obtained in the ANL-E laboratory. Information that will assist in judging the quality of the results includes

TABLE 7.2

Summary of DOE-EML-QAP Samples, 1999

Matrix	Constituent	Date	Unit	EML	ANL-E	Ratio	Comments
Air filter	Manganese-54	Sept.	Bq/filter	7.91	8.10	1.02	Acceptable
	Cobalt-57	March		3.01	3.25	1.08	Acceptable
		Sept.		7.73	8.03	1.04	Acceptable
	Cobalt-60	March		4.96	5.50	1.11	Warning
		Sept.		6.35	7.23	1.14	Warning
	Strontium-90	March		0.644	0.630	0.98	Acceptable
		Sept.		0.336	0.330	0.98	Acceptable
	Ruthenium-106	Sept.		5.50	8.25	1.50	Not Acceptable
	Antimony-125	March		3.59	4.28	1.19	Warning
	Cesium-137	March		6.05	6.59	1.09	Acceptable
		Sept.		6.43	6.45	1.00	Acceptable
	Uranium-234	March		0.060	0.066	1.10	Acceptable
		Sept.		0.066	0.070	1.06	Acceptable
	Uranium-238	March		0.061	0.063	1.03	Acceptable
		Sept.		0.065	0.070	1.08	Acceptable
	Plutonium-238	March		0.272	0.310	1.14	Acceptable
		Sept.		0.097	0.100	1.03	Acceptable
	Plutonium-239	March		0.124	0.140	1.13	Acceptable
		Sept.		0.136	0.140	1.03	Acceptable
	Americium-241	March		0.134	0.140	1.05	Acceptable
		Sept.		0.127	0.130	1.02	Acceptable
Soil	Potassium-40	March	Bq/kg	362.8	387.0	1.07	Acceptable
		Sept.		821.0	780.0	1.05	Acceptable
	Strontium-90	March		32.4	32.9	1.02	Acceptable
		Sept.		13.00	14.60	1.12	Acceptable
	Cesium-137	March		659.5	746.0	1.13	Acceptable
		Sept.		204.0	261.0	1.28	Warning
	Uranium-234	March		140.7	123.0	0.87	Acceptable
		Sept.		190.0	168.0	0.88	Acceptable
	Uranium-238	March		145.0	132.0	0.91	Acceptable
		Sept.		202.0	173.0	0.86	Acceptable
	Plutonium-239	March		8.11	8.48	1.04	Acceptable
		Sept.		3.20	2.94	0.92	Acceptable
	Americium-241	March		4.89	5.03	1.03	Acceptable
		Sept.		1.44	1.85	1.28	Acceptable

TABLE 7.2 (Cont.)

Matrix	Constituent	Date	Unit	EML	ANL-E	Ratio	Comments
Water	Hydrogen-3	March	Bq/L	121.1	129.0	1.06	Acceptable
		Sept.		80.7	82.4	1.02	Acceptable
	Cobalt-60	March		51.1	54.8	1.07	Acceptable
		Sept.		52.4	54.0	1.03	Acceptable
	Strontium-90	March		4.10	3.66	0.89	Acceptable
		Sept.		1.72	1.64	0.95	Acceptable
	Cesium-137	March		39.4	39.5	1.00	Acceptable
		Sept.		76.0	76.4	1.01	Acceptable
	Uranium-234	March		0.268	0.260	0.97	Acceptable
		Sept.		0.370	0.390	1.05	Acceptable
	Uranium-238	March		0.262	0.280	1.07	Acceptable
		Sept.		0.360	0.380	1.06	Acceptable
	Plutonium-238	March		0.772	0.790	1.02	Acceptable
		Sept.		0.790	0.800	1.01	Acceptable
	Plutonium-239	March		1.009	0.990	0.98	Acceptable
		Sept.		0.870	0.890	1.02	Acceptable
	Americium-241	March		1.146	1.230	1.07	Acceptable
		Sept.		0.850	0.940	1.11	Acceptable

the fact that typical uncertainties for ANL-E's analyses are 2 to 50%, and that the uncertainties in the EML results are 1 to 30% (depending on the nuclide and the amount present). For most analyses for which the differences are large (> 20%), the concentrations were quite low and the differences were within the measurement uncertainties.

Overall, the ANL-E performance in the EML intercomparison studies on the three matrices resulted in over 91% (48 out of 53) of the analysis being in the DOE-EML-QAP acceptable range. Four samples analyzed by gamma-ray spectrometry fell within the warning category, while one air filter sample analyzed for ruthenium-106 produced unacceptable results. The ANL-E performance on these samples indicated that the reported results are accurate.

7.3. Chemical Analysis

The documentation for nonradiological analyses is contained in the ESH-ASCL Procedure Manual. All samples for NPDES and groundwater are collected and analyzed in accordance with EPA regulations found in 40 CFR Part 136,[23] EPA-600/4-84-017,[30] and SW-846.[8]

Standard reference materials traceable to the NIST exist for most inorganic analyses (see Table 7.3) and are replaced annually. Detection limits are determined with techniques listed in 40 CFR Part 136[23] and are given in Table 7.4. In general, the detection limit is the measure of the variability of a standard material measurement at 5 to 10 times the instrument detection limit as measured over an extended time period. Recovery of inorganic metals, as determined by "spiking" unknown solutions, must be within the range of 75 to 125%. The precision, as determined by analysis of duplicate samples, must be within 20%. These measurements must be taken for at least 10% of the samples. Comparison samples for organic constituents were formerly available from the EPA; they are now commercially available under the Cooperative Research and Development Agreement that exists between the EPA and commercial laboratories. In addition, standards are available that are certified by the American Association for Laboratory Accreditation, under a Memorandum of Understanding with the EPA. Many of these standards were used in this work. At least one standard mixture is analyzed each month; Tables 7.5 and 7.6 show the 1999 results for VOCs and SVOCs, respectively. The recoveries listed are those required by the respective methods.

7.4. NPDES Analytical Quality Assurance

ANL-E conducts the majority of the analyses required for inclusion in the DMR. These analyses are conducted in accordance with EPA-approved methods set out in 40 CFR Part 136.[23] To demonstrate the capabilities of the ANL-E laboratory for these analyses, the EPA requires that ANL-E participate in the DMR Quality Assurance program. The EPA sends a series of intercomparison samples to ANL-E annually, and the ensuing analytical results are submitted to the EPA for review. The proficiency of the laboratory is determined by comparing the analytical results for the submitted samples with the EPA values. The ANL-E laboratory has consistently performed very well on these tests. In 1999, the EPA decided to privatize the preparation of the intercomparison samples. Because of delays in accrediting providers, the EPA decided to cancel the DMR Quality Assurance Program for 1999. The EPA plans to resume this program in 2000.

TABLE 7.3

Standard Reference Materials Used for Inorganic Analysis

Constituent	Reference Material[a]
Antimony	HPS-10002-2
Arsenic	HPS-10003-1
Barium	HPS-10004-1
Beryllium	HPS-10005-1
Boron	HPS-10007-4
Cadmium	HPS-10008-1
Chromium	HPS-100012-1
Cobalt	HPS-100013-1
Copper	HPS-100014-1
Iron	HPS-100026-1
Lead	HPS-100028-1
Manganese	HPS-100032-1
Mercury	HPS-100033-1
Nickel	HPS-100036-1
Selenium	HPS-100049-1
Silver	HPS-100051-1
Thallium	HPS-100058-1
Vanadium	HPS-100065-1
Zinc	HPS-100068-1
Sulfate	NIST-SRM 3181
Chloride	NIST-SRM 3182
Fluoride	NIST-SRM 3183

[a] HPS = High Purity Standards, Inc.; NIST-SRM = National Institute of Standards and Technology - Standard Reference Materials.

TABLE 7.4

Detection Limit for Metals Analysis, 1999

	Detection Limit (mg/L)	
Constituent	AA[a]	ICP[b]
Antimony	0.0030	NA[c]
Arsenic	0.0025	0.124
Barium	NA	0.023
Beryllium	0.0002	0.019
Boron	NA	0.023
Cadmium	0.0002	0.012
Chromium	0.015	0.020
Cobalt	0.025	0.018
Copper	0.005	0.016
Hexavalent chromium[d]	0.006	NA
Iron	0.025	0.019
Lead	0.0020	0.072
Manganese	0.015	0.018
Mercury	0.0001	NA
Nickel	0.020	0.031
Selenium	0.0030	0.118
Silver	0.0005	NA
Thallium	0.0015	0.068
Vanadium	NA	0.035
Zinc	0.005	0.011

[a] AA = Atomic Absorption Spectroscopy.

[b] ICP = Inductively Coupled Plasma-Atomic Emission Spectroscopy.

[c] NA = not analyzed.

[d] Calorimetric measurement.

TABLE 7.5

Quality Check Sample Results: Volatile Analyses, 1999

Constituent	Recovery[a] (%)	Quality Limit (%)
Benzene	108	73 – 126
Bromobenzene	105	76 – 133
Bromodichloromethane	97	101 – 138
Bromoform	60	57 – 156
Butylbenzene	110	71 – 125
sec-Butylbenzene	84	71 – 145
t-Butylbenzene	96	69 – 134
Carbon Tetrachloride	103	86 – 118
Chlorobenzene	101	80 – 137
Chloroform	116	68 – 120
o-Chlorotoluene	116	81 – 146
p-Chlorotoluene	101	73 – 144
1,2-Dibromo-3-chloropropane	64	36 – 154
Dibromochloromethane	81	68 – 130
1,2-Dibromoethane	112	75 – 149
Dibromomethane	95	65 – 143
1,2-Dichlorobenzene	115	59 – 174
1,3-Dichlorobenzene	105	84 – 143
1,4-Dichlorobenzene	106	58 – 172
1,1-Dichloroethane	116	71 – 142
1,2-Dichloroethane	111	70 – 134
1,1-Dichloroethene	95	18 – 209
cis-1,2-Dichloroethene	113	85 – 124
trans-1,2-Dichloroethene	105	67 – 141
1,2-Dichloropropane	100	19 – 179
1,3-Dichloropropane	112	73 – 145
1,1-Dichloropropene	94	71 – 133
Ethyl Benzene	95	84 – 130
Isopropylbenzene	98	70 – 144
4-Isopropyltoluene	103	72 – 140
Methylene Chloride	113	D – 197[b]
n-Propylbenzene	94	78 – 139
1,1,1,2-Tetrachloroethane	96	88 – 133
Tetrachloroethene	112	84 – 132
Toluene	112	81 – 130
1,1,1-Trichloroethane	110	68 – 149
1,1,2-Trichloroethane	101	70 – 133
Trichloroethene	113	91 – 135
1,2,3-Trichloropropane	101	50 – 158
1,2,4-Trimethylbenzene	89	80 – 144
1,3,5-Trimethylbenzene	92	76 – 142
o-Xylene	112	79 – 141
p-Xylene	90	74 – 138

[a] Average of two determinations.

[b] D denotes that the compound was detected.

TABLE 7.6

Quality Check Sample Results:
Semivolatile Analyses, 1999

Constituent	Recovery[a] (%)	Quality Limit (%)
2-Fluorophenol[b]	56.1	21 – 100
Phenol-d5[b]	44.2	10 – 94
Phenol	44.7	17 – 100
2-Chlorophenol	85.7	36 – 120
1,4-Dichlorobenzene	56.2	37 – 106
n-Nitroso-n-Propylamine	50.2	24 – 198
Nitrobenzene-d5[b]	79.8	35 – 114
1,2,4-Trichlorobenzene	65.8	57 – 129
4-Chloro-3-Methylphenol	92.0	41 – 128
2-Fluorobiphenyl[b]	87.1	43 – 116
Acenaphthene	91.2	47 – 145
2,4-Dinitrotoluene	88.9	48 – 127
2,4,6-Tribromophenol[b]	79.2	10 – 123
Pentachlorophenol	109.0	38 – 152
Pyrene	88.4	70 – 100
Terphenyl-d14[b]	92.2	33 – 141

[a] Average of three determinations.

[b] Required surrogates.